

The Status of and Challenges in CdTe Thin-Film Solar-Cell Technology

Alvin D. Compaan
Department of Physics and Astronomy,
The University of Toledo,
Toledo, OH, 43606, USA

ABSTRACT

Polycrystalline CdTe thin-film solar cells have shown high potential for low cost, large-area module fabrication. But successful large-scale commercial production has been elusive. Fabrication of the basic n-CdS / p-CdTe heterojunction is possible by a wide variety of methods, including close-spaced sublimation, vapor-transport deposition, electrodeposition, chemical bath deposition, and magnetron sputtering. An overview of these methods is presented as well as the role of the postdeposition "activation" treatment using CdCl₂ and issues related to the difficulty of obtaining low resistance back contacts to CdTe. We present some of our recent fabrication results using rf magnetron sputtering and discuss some of the advantages that appear possible from the use of sputtering methods in this class of materials. Some of these advantages are particularly relevant as the polycrystalline thin-film PV community addresses the challenges of fabricating tandem cells with efficiencies over 25%.

INTRODUCTION

In the context of this symposium focused on amorphous and nanocrystalline silicon it is useful to set the environment for polycrystalline thin-film solar cells, particularly CdTe, in the broader field of photovoltaics, both traditional crystalline as well as amorphous thin film.

The efficiencies of the laboratory best photovoltaic (PV) cells have shown steady advances over the past two decades so that triple-junction, epitaxially grown III-V semiconductor-based cells have reached efficiencies (at air mass 1.5 global) of about 34%, [1] single-crystal Si cells with precise texturing of the surface and buried grid lines have reached ~24% efficiency, [2] and multicrystal Si grown by ingot casting has reached ~18%. [2,3] In addition, there are three competitive inorganic thin-film technologies which have achieved efficiencies well above 10%. These are: CuIn(Ga)Se₂ with an efficiency of 19.8%, CdTe (16.5%), and amorphous silicon (12% stabilized). [4] However, in most applications the cost per peak watt is more important than utilizing cells with the highest efficiency and thus the thin-film technologies appear to be quite viable commercially, although thin-film PV manufacturing has not generally achieved profitable high-volume production.

As the production of PV has increased, the cost has fallen. Analyses by Margolis [5] and by Surek [6] have shown that the retail cost of solar panels has closely followed an 80% learning curve since the beginning of cost tracking in 1976. Thus for every doubling in cumulative production the cost has dropped to 80% of the previous cost. (For example, the cost of modules has dropped from ~\$70/W_p in 1976 to ~\$7/W_p in 1992 to under \$3/W_p in 2002.) Today the traditional crystalline (and multicrystalline silicon) accounts for about 80% of PV production and sales. However, Surek has predicted that for a variety of reasons, the cost of silicon-based PV cannot continue declining much longer. Other analysts are more optimistic about the possibility of silicon-based cells to continue the cost reductions and one form that may permit cost

reductions is thin silicon on ceramic or glass substrates. Another may be “ribbon” silicon drawn from the melt in a hexagonal form or edge-defined between wires.

Many analysts anticipate that one or more of the thin-film technologies will lead the way in providing cost reductions that may, in the foreseeable future, yield modules approaching \$0.50 per peak watt for PV panel manufacturing cost. The status of thin-film amorphous Si PV is extensively covered in this symposium. The status of polycrystalline thin-film CIGS is the subject of another paper in this symposium and the status of dye-sensitized nanocrystalline PV the subject of another. Our focus in this paper is to review the status of and challenges in the field of II-VI semiconductor heterojunction CdS/CdTe solar cells.

As identified above, two of the most promising types of thin-film solar-cell materials are polycrystalline. Copper, indium, and selenium are often alloyed with Ga and/or S to yield $\text{CuIn}(\text{Ga})[\text{Se}(\text{S})_2]$ to yield easily the record efficiency (19.8%) for any thin film PV material[4] Cadmium telluride, CdTe, has the second highest efficiency for the thin films at 16.5%.[4] Both materials are naturally p-type due to small deviations from stoichiometry and form excellent heterojunctions with the wider bandgap semiconductor, CdS, which is naturally n-type. For the CdS/CdTe system there is a ~10% lattice mismatch and a structural difference between the wurtzite CdS and the zincblende CdTe. Nevertheless, these materials form a junction with remarkably good electronic properties, possibly due to some interdiffusion.

Whereas the a-Si:H is complicated by the existence of dangling bonds, the polycrystalline thin films are complicated by the existence of grain boundaries which can introduce large densities of defects and provide recombination centers that greatly shorten the minority carrier lifetimes in the grains. Thus, one of the key features of these two materials is the fact that the grain boundaries either are naturally passive or can be passivated with relatively simple procedures. (The fact that the III-V materials, such as GaAs, which work so well as single-crystal materials, have yet to show much promise as polycrystalline thin-film PV materials is most likely due to the difficulty of achieving good grain boundary passivation in this class of materials.) Recently, Persson and Zunger[7] have proposed that the key to effective grain boundary passivation in CuInSe_2 is the presence of Cu-vacancy surface reconstruction at the grain boundaries (GBs) of this material which leads to an energy barrier for holes. They suggest that this barrier together with the segregation of impurities to the GBs accounts for the superior performance of the polycrystalline CIGS compared with the single crystal material.

In the case of CdTe, we have recently completed x-ray fine structure measurements which suggest that in sputtered cells prepared with typical amounts of Cu at the back contact, most of the Cu ends up bound with oxygen and at grain boundaries.[8] Further details are given later. Many of the important issues that determine the efficiency of the polycrystalline CdTe thin-film solar cells are discussed in more detail below.

THE CdS/CdTe CELL STRUCTURE

The binary polycrystalline semiconductor CdTe has the ideal band gap match ($E_g=1.5$ eV at room temperature) to the terrestrial solar spectrum. Furthermore it has a direct band gap with absorption coefficient that quickly rises to $\alpha = 10^4 \text{ cm}^{-1}$ for photon energies above 1.7 eV. Although CdTe can be doped both p-type and n-type, the best junctions for CdTe solar cells have not been homojunctions but have been formed as heterojunctions with CdS which is preferentially n-type. Since CdS has a band gap of 2.4 eV, an n-type CdS on p-type CdTe cell



Fig. 1 Structure of typical CdTe superstrate cell. Typically the back contact is a metal or carbon paste rather than the transparent ZnTe shown here.

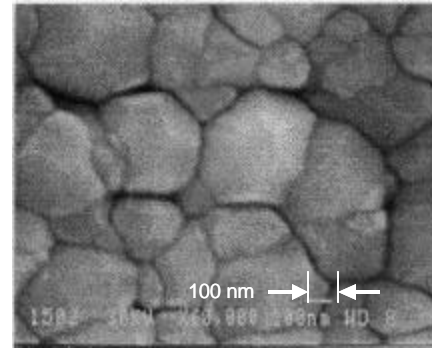


Fig. 2 SEM micrograph of a sputtered CdTe layer 2 μm thick.

configuration is used. This allows for the wider bandgap partner to serve as the window layer. Unfortunately, apparently in all devices reported to date, the minority carrier (hole) lifetime of the CdS is too low for any significant carrier collection from the CdS. Thus much effort has gone in to fabricating cells with very thin CdS that will allow most of the photons with $h\nu > 2.4$ eV to pass into the CdTe.

Most solar cells are fabricated in a configuration that permits the junction to be made last followed by a minimum of further processing (usually only the transparent conductor and grid lines). However, in the case of CdTe, the best cells have been made in the inverted configuration with the transparent conductor formed first and then the CdS/CdTe junction followed by the rest of the absorber layer and the back contact. This yields the "superstrate" configuration in which the cell is operated with the glass/TCO/ CdS facing the sun. See Fig. 1. Fabricating the critically important junction first seems counterintuitive until one realizes that the CdTe is a material with high electron affinity ($\chi_A = 4.28$ eV) so that a back contact to the p-type CdTe would require a material (usually metal) with a work function of $W = \chi_A + E_g \sim 5.78$ eV to achieve flat-band conditions appropriate for hole transport. There are no common metals that satisfy this criterion. The second approach is to fabricate a heavily doped CdTe layer at the back contact to allow for tunneling.

The sketch of Fig. 1 shows the inclusion of a high resistivity transparent (HRT) layer between the TCO and the CdS and is discussed in the section on front contacts below. Fig. 1 also shows the use of ZnTe, which is not the standard back contact but has been investigated by Gessert, et al[9] as part of a dry contact process with Cu doping and by us as part of a copper free and transparent back contact for possible use in tandem cell applications.[10] Further discussion of this critically important CdTe back contact formation are discussed below.

CdTe and CdS DEPOSITION METHODS

CdTe appears to be unique among the photovoltaic materials in the variety of deposition methods that have been successfully used to deposit the junction. The CdS layer can be deposited by close-spaced sublimation (CSS), vapor transport-deposition (VTD), magnetron sputtering (MS), and chemical bath deposition (CBD). The CdTe layers have been deposited by CSS, VTD, and MS as well as by spray pyrolysis, screen printing, electrodeposition, physical vapor deposition, and MOCVD.[4] All of these methods have yielded cells with performance

well above 10% and several of these above 14%. This unparalleled flexibility in available deposition methods arises undoubtedly from the stability of the binary compounds and their tendency to self compensate with intrinsic defects to form quite stable p-type CdTe and n-type CdS. The second factor which allows for such a wide range of deposition methods, undoubtedly arises from the ubiquitous application of a post-deposition activation treatment which involves an anneal step at 400 ± 15 °C in the presence of some O₂. The various deposition methods fall into three substrate deposition temperature ranges. The highest temperatures have yielded the best performance cells and have utilized borosilicate glass with substrate temperature up to 650 °C. Because of the high cost of this glass, however, commercial scale systems have used soda lime glass with temperatures limited to ~550 °C. (First Solar, Antec Solar, Golden Photon, Mitsubishi).[4] PVD, MOCVD, and sputtering have used intermediate temperatures, typically 250 to 350 °C. Finally, electrodeposition is performed at about 90 °C.

However, independent of the substrate deposition temperature, a postdeposition chloride treatment is used to fully activate the material. (The Mitsubishi process is somewhat different in that the chloride is introduced into the screen-printed precursors which are then sintered at temperatures presumably equivalent to the normal CdCl₂ process.) This activation process is not fully understood but there are likely to be three important ingredients: 1) the extra Cd may be important to control the stoichiometry, 2) the chlorine is undoubtedly playing a role in defect compensation, and 3) finally, the oxygen in the air or He/O₂ or Ar/O₂ atmospheres during the chloride process is probably active, perhaps in conjunction with the Cl, in passivating the grain boundaries. Further discussion of this is given in the section on "Grain boundaries" below.

In the following discussion, we will consider in more detail three principal areas of active study. These are the front contact and window layer, the back contact to the CdTe, and the absorber layer including grain boundaries.

FRONT CONTACT/WINDOW LAYER

Manufactured panels are based typically on 3 mm soda lime glass for cost reasons but the transmission is reduced largely because of residual iron absorption. Fluorine-doped tin oxide (SnO₂:F) is manufactured in large quantities and has served as the starting substrate material also for much research work, including our own. The highest efficiency laboratory cells, however, are made on 1 mm borosilicate or aluminosilicate glass which has better transmission and can be taken to higher deposition temperatures. Several groups have used their own transparent conducting oxide (TCO) including SnO₂:F, cadmium stannate (Cd₂SnO₄), indium tin oxide (ITO), and ZnO:Al.

For the highest efficiencies, the TCO is perhaps less important than the use of a high resistivity buffer layer between the TCO and the n-CdS. This may be composed of an undoped layer of SnO₂, used to produce 15.8% efficient devices,[11] or zinc stannate (Zn₂SnO₄) which was used together with cadmium stannate to produce the current record cell of 16.5%.[12] Typically these buffer layers are fabricated with resistivity of 1-10 kΩ/□ and can provide protection from shunting if the CdS has pinholes. (See additional discussion of weak diodes and nonuniformity below.) This becomes especially important when thinner layers of CdS are used to improve the blue response of the cell. With CdS layers of 0.15 μm or greater there appears to be little need for the use of this buffer layer, but higher cell currents can be achieved with CdS layers of 50 nm or less. With such thin CdS, the open-circuit voltage typically is substantially

reduced without the use of this high resistivity buffer layer. A recent model, in addition, has proposed that the high resistivity buffer layer can play a key role in the operation of the cell. This is consistent with the observations that a certain amount of copper can improve the operation of a cell by compensating the n-type doping of the CdS to make the CdS itself more resistive.

BACK CONTACTS TO CdTe

With one of the highest metal work functions of 5.2 eV, gold still does not satisfy the work function suggested by the electron affinity plus band gap energy of CdTe. Thus essentially all successful stable back contacts to CdTe have involved the use of copper to create a heavily doped layer next to the metal. However, Cu is notorious for being a fast diffuser in semiconductors such as Si. This presents somewhat of a dilemma for fabricating back contacts to CdTe and it has been found that some form of chemical etching of the CdTe surface prior to application of the back contact is usually required. Thus, an "N-P" etch (nitric-phosphoric acid) is often used. The N-P etch or Br-methanol etch leaves a Te-rich layer on the CdTe. Typically the more aggressive etches can only be used with relatively thick CdTe layers (5-10 μm). The NREL group has shown that some distance along the grain boundaries below the back contact is also very rich in Te. The back contact yielding the highest performance has been a carbon paste mixed with HgTe doped with Cu. During the back contact application, a modest heat treatment is used to remove the volatiles and probably to drive some diffusion of Cu into the CdTe. In our relatively thin (2-2.5 μm CdTe) sputtered cells, we have avoided using any etch or wet rinse, and have successfully used very thin evaporated Cu (3 nm) followed by evaporated Au (10-20 nm). We find that it is important to control the Cu thickness very carefully for these thin CdTe cells.

It is generally accepted that one of the beneficial effects of creating a Te layer at the back surface is to facilitate the forming of a Cu_{2-x}Te layer which then can serve to retain Cu at the back contact and inhibit diffusion toward the junction. Weak etches may have the effect of creating a Te-rich (or equivalently a Cd-poor) CdTe layer at the back which can facilitate enhanced p-type doping since the Cd vacancy is a double acceptor (although it is a relatively deep acceptor with transitions at 120 (0/-) and 270 meV (-/2-) above the valence band).[13] Furthermore the Cd vacancy paired with a substitutional Cl_{Te} forms the A-center which can be an effective acceptor at about $E_{\text{V}} + 120$ meV.[14]

MAGNETRON SPUTTERING FOR CdS/CdTe SOLAR CELLS

Although the deposition over large areas of polycrystalline thin-film semiconductors such as CdTe is possible by a variety of methods, the use of a plasma-based method such as magnetron sputtering can have significant advantages.

Earlier we reported sputtered cells with efficiency up to 11.6% on soda-lime glass (SLG) with a commercial coating of $\text{SnO}_2:\text{F}$. [15] This substrate material (both the glass, with its relatively high content of iron, and the tin oxide) is known to have limitations in transparency and has less than optimum texture. Nevertheless, a good supply of inexpensive substrate material is readily available and convenient. Most of our effort has been focused on this starting substrate material. Recently we have made slight adjustments in our process and have improved

the cell performance on these 2 mm thick commercial substrates to 12.6% as measured at NREL. More recently, we have added the capability of magnetron sputtering of doped ZnO:Al with the dual objectives of depositing our own TCO and of fabricating a recombination junction. (See below.)

The ZnO:Al films were deposited using RF magnetron sputtering from a ceramic ZnO:Al₂O₃ (2%) target at 220 °C on 1 mm thick, ultrasonically alkaline-soap-cleaned aluminosilicate (ASG) glass slides. The depositions were carried out in pure argon gas at 48 W of RF power and 10-12 mTorr pressure. The deposition rate was $\sim 2 \text{ \AA/sec}$. We have used this sputtered ZnO:Al as the TCO layer to fabricate cells with sputtered CdS and CdTe layers. The structure of these cells was: 1 mm aluminosilicate glass/1.5 μm ZnO:Al/0.13 μm CdS/2.3 μm CdTe/3nm Cu/20nm Au similar to that used for the 12.6% device on TEC-7 except for the use of the 1mm thick aluminosilicate glass (Corning 1737) substrate and our sputtered TCO layer of ZnO:Al. All subsequent deposition/processing of the CdTe and back contact was the same, as well as the 387 °C vapor-CdCl₂ treatment. Note that no water rinse or chemical treatment including etching was used after the initial glass cleaning. The metal back contacts were evaporated through a mask of 0.15 cm² holes followed by diffusion at 150 °C in air.

The standard tests at NREL gave $V_{OC}=814\pm 1 \text{ mV}$, $J_{SC}=23.6\pm 0.1 \text{ mA/cm}^2$, fill factor = 73.25 ± 0.2 , and efficiency (?) = $14.0\pm 0.2\%$ (air mass 1.5). This is a 14% increase in current relative to our best cell on TEC-7 which was tested at $V_{OC}=820 \text{ mV}$, $J_{SC}=20.7 \text{ mA/cm}^2$, FF=74%, and ? = $12.6\pm 0.2\%$. The NREL test results are summarized in Fig. 3.[16]

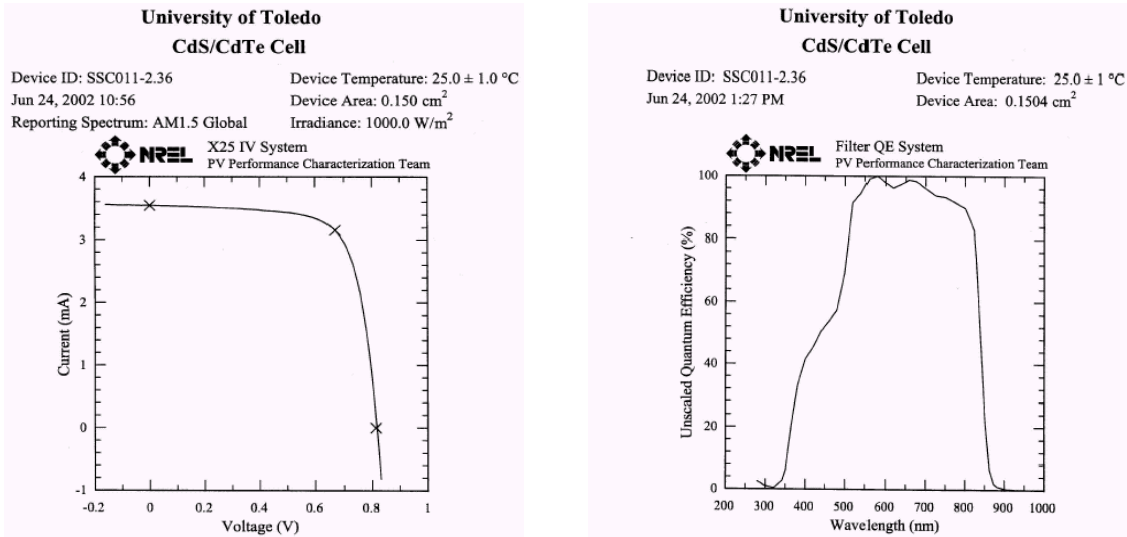


Fig. 3. I-V and quantum efficiency test results from NREL of 14% efficient all-sputtered, polycrystalline thin-film ASG/ZnO:Al/CdS/CdTe cells.

One of the most interesting features of this cell structure is that the ZnO works at all. ZnO:Al has high transparency well into the infrared and excellent sheet resistance with high mobility. Thus it is an attractive candidate as a TCO. However, although ZnO:Al has been used very successfully as the final layer in substrate-configuration cells such as copper-indium-gallium-diselenide (CIGS) in which it is the final deposited layer, attempts to utilize it as the TCO in superstrate configuration cells such as CdTe, during which it is subjected to subsequent high-temperature processing, have not been very successful. The best previously reported efficiency of a ZnO/CdS/CdTe device was $\sim 9\%$ [17] compared to 14% [18] for SnO₂:F TCO on

SLG. The limited efficiency previously experienced with ZnO:Al may be due to its thermal instability at high growth/processing temperature (*e.g.*, close-spaced-sublimation (CSS) or vapor-transport-deposition (VTD) techniques) and its instability in high acidic or basic media (*i.e.*, solution growth or electro-deposition techniques). Thus, since close-spaced sublimation and vapor transport deposition of CdTe typically reach temperatures of 550 to 650 °C, the ZnO:Al degrades. Our results thus indicate that the use of sputtering for the deposition of the CdS and CdTe layers can allow the use of this very attractive TCO. In our case, deposition of the CdS and CdTe was done 250 °C. The highest temperatures were reached during the vapor CdCl₂ treatment at 387 °C. This result confirms that the moderate temperatures possible with magnetron sputtering can provide important advantages in cell fabrication and expand the range of materials available for thin-film polycrystalline solar cells.

GRAIN BOUNDARIES IN CdTe CELLS

The SEM micrograph of Fig. 2 shows the length scales appropriate for the relatively small grain material produced in the magnetron-sputtered (or electrodeposited) CdTe. Remarkably, however, the performance of polycrystalline CdS/CdTe cells appears not to be affected much by the grain size. This indicates that grain boundaries are effectively passivated during the CdTe growth or processing. In recent high resolution x-ray fine structure studies at the MR-CAT beamline at the Argon Advanced Photon Source we have found some indirect evidence that suggests the origin of this passivation. As mentioned above, our back contact typically uses 3 nm of Cu at the back surface of ~2 μm of CdTe. If all of the Cu were evenly diffused through the CdTe, one could expect a Cu density of ~10²⁰ cm⁻³. However, C-V measurements of CdTe cells from several laboratories indicate the maximum acceptor densities in CdTe of ~5×10¹⁴. Thus most of the Cu is inactive. The goal of our measurements was to identify the lattice location of most of the Cu in CdTe.

X-ray absorption fine structure (XAFS) is a powerful for understanding the lattice environment around designated element atoms. By using the fine structure in the Cu K-edge x-ray absorption spectrum we can elucidate the predominant lattice location of Cu in polycrystalline, thin-film CdTe solar cells. In particular, we have studied how the typical CdCl₂ vapor treatment in dry air changes the local environment of the Cu subsequently diffused into CdTe. Our x-ray absorption fine structure measurements lead to the conclusion that films which received the Cu diffusion having no prior treatment with CdCl₂ appear to show the Cu mostly

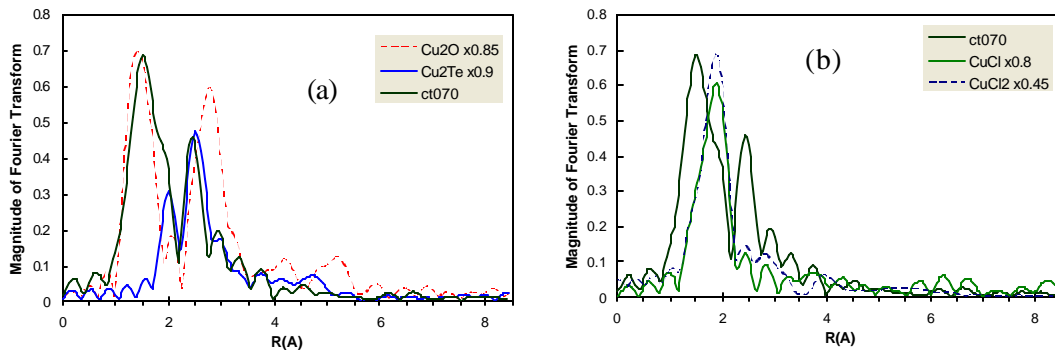


Fig. 4. a) Radial Distribution Function of CdCl₂ treated CdTe:Cu with long diffusion (ct070), Cu₂O and Cu₂Te; b) RDF comparison of CdTe:Cu (ct070) with CuCl and CuCl₂.

bound with Te similar to Cu_2Te . *However*, if the film has received the CdCl_2 treatment, *which for cells is always done in the presence of some O_2* , then the Cu appears to be bound not with Cl but with O.[19]

We also observed that the features similar to Cu_2O in CdCl_2 treated CdTe films are removable by selective HCl acid etching. After 10 seconds etching in 9% HCl acid, most remaining copper is found to be bound with Te as in non-chloride-treated CdTe films, with a small portion of copper bound with O as CuO, instead of Cu_2O . This is consistent with the much higher etch rates of Cu_2O compared with CuO and Cu_2Te in HCl.

The radial distribution function (RDF) the CdTe:Cu film diffused after CdCl_2 treatment confirms that most copper is bound with oxygen as Cu_2O in the CdTe film. As shown in Fig 4a, the major peak at 1.50\AA locates the 1st neighbor shell around the copper atoms, which is only a small shift from the 1st neighbor shell of the Cu_2O reference at 1.44\AA . However some of the copper in the film appears to be bound with Te, as shown by the peak at 2.45\AA and the shoulder of the 1.5\AA peak which are the two strongest peaks of Cu_2Te in Fig 4a. As a further check we show the RDF of CuCl and CuCl_2 . The RDF of CuCl, Fig. 4b, shows a similar bond length and structure to CuCl_2 except for a weaker magnitude of scattering, which is reasonable for the smaller coordination number to copper in CuCl. Thus, neither CuCl nor CuCl_2 is found to have similar bond lengths as the CdCl_2 -treated CdTe:Cu films. Although the XFS data are not spatially resolved to conclusively indicate grain boundaries as the location of the Cu_2O , the fact that the band gap of Cu_2O is 2.0 eV supports the suggestion that this semiconductor may be playing an important role in the passivation of grain boundaries in CdTe ($E_g=1.5$ eV) which has received the CdCl_2 activation treatment.

NONUNIFORMITY ISSUES IN CdTe CELLS

All thin-film electronic devices and especially polycrystalline thin-film solar cells have inherent lateral nonuniformities. Grain size variations, thickness variations of one or more of the layers, interfacial oxides, contamination, pinholes, and other "weaknesses"...all almost certainly contribute to nonuniformities. Because of the presence of junctions and barriers many of these nonuniformities are exponentially sensitive to lateral variations. The presence of back barriers was suggested above in our discussion of the difficulties of contacting CdTe. Fig. 5 is a sketch of the band bending and back barrier for holes believed to be typical in CdTe cells. Fig. 6 illustrates the I-V curves for the normal strong diode and a weak diode with a significantly lower V_{OC} . This weak diode will be driven into strong forward bias by the surrounding "normal" diodes when all are irradiated. As a consequence, the weak diode can serve as a strong current shunt. Karpov, et al,[20] have shown that in two dimensions the weak diode will affect an area given by the screening length, L_o ,

$$L_o = [kT/ej_o?]^{1/2}, \quad (1)$$

where T is the temperature, j_o is the current density and ? is the sheet resistance of the more resistive layer (either above or below the diode) linking the diodes. This analysis suggests that the effects of the inevitable weak diodes can be minimized by introducing a more resistive layer at the front or back of the solar cells.

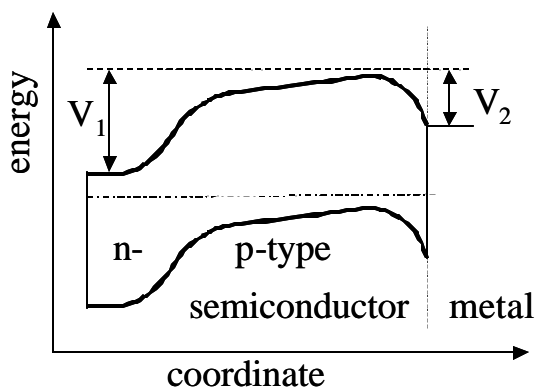


Fig. 5 Schematic band diagram of the CdS/CdTe cell emphasizing the presence of a hole barrier, V_2 , at the back contact typically ~ 30 meV.

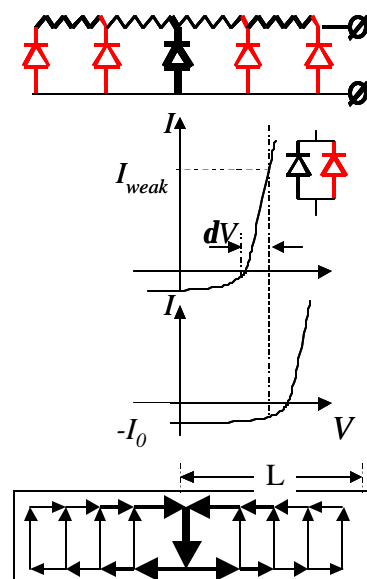


Fig. 6 Elements of a random diode model which can result from variations in the back barrier leading to weak diodes which can shunt large amounts of current if the diodes are strongly linked with low resistance paths.

POLYCRYSTALLINE II-VI TANDEM CELLS—A BEGINNING

Another example of the flexibility inherent in the use of magnetron sputtering is the capability of doping II-VI films during sputtering. This we have demonstrated in studies of nitrogen-doped ZnTe. ZnTe:N films ~ 750 nm thick were deposited by reactive rf sputtering at ~ 350 C with 3% N_2 in the Ar sputter gas on aluminosilicate glass.[21] Films were characterized before and after annealing to determine changes in structure, optical, and electrical properties. Surface morphology and grain size were determined using atomic force microscopy and scanning electron microscopy. The crystalline properties of the films were determined by x-ray diffraction. Cross-grain film sheet resistance, measured by a 4-point probe, was $\sim 10 \Omega/\square$ for a $1 \mu\text{m}$ film. Studies of the temperature stability of these films indicate their resistivity decreases by about a factor of two after a 30 minute heat treatment in air (presumably due to grain boundary changes) but are stable thereafter while heated in air, nitrogen or argon to above 350 C.

In order to examine the suitability of the p-type ZnTe:N and n-type ZnO:Al to form a transparent back contact or a transparent recombination junction for polycrystalline II-VI solar cells, we

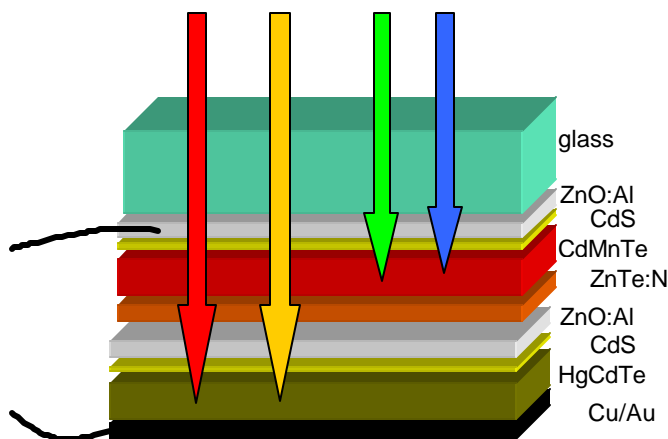


Fig. 7 Two-terminal tandem cell based on CdMnTe and HgCdTe absorbers

fabricated several recombination junction structures on SnO₂:F-coated Tec 7 glass. Initial attempts to make the structures on uncoated glass substrates failed due to poor adhesion to the glass of the bottom metal electrode. The completed structures consist of 0.30 μm Ni on the SnO₂:F coated glass, 0.16 μm ZnTe:N, 0.25 μm ZnO:Al, and 0.32 μm Al. The resulting structure exhibited a contact resistance of $\sim 3 \Omega\text{-cm}^2$ adequate for a junction/recombination interconnect junction.[22]

We have incorporated the ZnTe:N/ZnO:Al recombination junction into a prototype tandem device based on a top cell of CdTe and a bottom cell of HgCdTe. We have prepared the tandem structure in the form shown in Fig. 7, using CdTe for the top cell (1.5 eV) and a bottom cell composition of $\sim 18\%$ Hg to reach $E_g \sim 0.95$ eV. Although the results are quite preliminary, we have demonstrated that an operational tandem device can be fabricated of these materials in a monolithic structure by magnetron sputtering. We have found a quantum efficiency response covering the range from about 400 nm to 1000 nm, and an open-circuit voltage of 0.9 V indicating voltage addition of the two junctions.[23]

SUMMARY

Much effort will be required to reach the 25% efficiency goal for polycrystalline tandems. It will require optimizing the electronic properties of the materials, grain boundary passivation, and film thicknesses to achieve current matching in the top and bottom junctions. However, the polycrystalline thin-film semiconductors clearly have major potential for reducing the cost of PV-generation to compete effectively with other, more traditional sources of electricity.

ACKNOWLEDGMENTS

This work has been supported primarily by NREL through the High Performance PV Program (Martha Symko-Davies) and also through the Thin Film Partnership Program of NREL (Ken Zweibel). The UT work referenced in this paper reflects the diligent efforts of faculty colleagues (Victor Karpov) postdocs (A. Gupta, D. Shvydka, S-H. Lee, and S.L. Wang) and students (X. Liu, J. Drayton, V. Parikh, A. Vasko, V. Plotnikov, and A. Korostyshevsky).

REFERENCES

- [1] J.M. Olson, D.J. Friedman, and S. Kurtz, in *Handbook of Photovoltaic Science and Engineering*, ed by A. Luque and S. Hegedus, Wiley, 2003, pp. 359-407.
- [2] I. Tobias, C. del Canizo, and J. Alonso, in *Handbook of Photovoltaic Science and Engineering*, ed by A. Luque and S. Hegedus, Wiley, 2003, pp. 255-303
- [3] A variety of data on PV efficiencies and production is available at <http://www.nrel.gov/solar/>
- [4] A very recent review of CI(G)S, CdTe, and a-Si cells can be found in articles, respectively by Shafarman and Stolt, McCandless and Sites, and by Deng and Schiff, in *Handbook of Photovoltaic Science and Engineering*, ed by A. Luque and S. Hegedus, Wiley, 2003.

- [5] Robert M. Margolis, "Experience Curves and Photovoltaic Technology Policy at the Human Dimensions of Global Change Seminar," Carnegie Mellon University, October 16, 2002
- [6] Tom Surek, Third World Conf. on PV Energy Conversion, Osaka, May, 2003, paper 8PLE301.
- [7] C. Persson and A. Zunger, Appl. Phys. Ltrs, Feb. 2004.
- [8] Xiangxin Liu, A.D. Compaan, N. Leyarovska, and J. Terry, Mat. Res. Soc. Symp. Proc. **763**, paper B3.5, (2003)
- [9] T. Gessert, A. Duda, S. Asher, C. Narayanswamy, C. Rose, 28th IEEE Photovoltaic Specialists Conf.—2000, pp. 654-7
- [10] J. Drayton, A. Gupta, K. Makhratchev, K.J. Price, R.G. Bohn, and A.D. Compaan, "Properties of RF Sputtered ZnTe:N for Back Contact to CdS/CdTe Solar Cells," Mat. Res. Soc. Symp. Proc. **668**, H5.9.1 (2001)
- [11] J. Britt and C. Ferekides, "Thin-film CdS/CdTe solar cell with 15.8% efficiency," Appl. Phys. Lett **62**, 2851 (1993).
- [12] X. Wu, et al, 17th European Photovoltaic Solar Energy Conference, 995 (2000).
- [13] Su-Huai Wei, S.B. Zhang, and Alex Zunger, J. Appl. Phys, **87**, 1304 (2000)
- [14] E. Molva, J.L. Pautrat, K. Saminadayar, G. Milchberg, N. Magnea, Phys. Rev. B **30**, 3344-54 (1984); A. Castaldini, A. Cavalini, and B. Fraboni, Appl. Phys. Lett. **69**, 3510 (1996).
- [15] M. Shao, A. Fischer, D. Grecu, U. Jayamaha, E. Bykov, G. Contreras-Puente, R.G. Bohn, and A.D. Compaan, Appl. Phys. Lett. **69**, 3045-3047 (1996).
- [16] Akhlesh Gupta and Alvin D. Compaan, Mat. Res. Soc. Symp. Proc. **763**, 161-4 (2003).
- [17] Y. Igasaki and H. Saito, J. Appl. Phys., **70**, 3613 (1991); A.N. Tiwari, A. Romero, D. Baetzner and H. Zogg, Prog. Res. Appl. **9**, 211 (2001)
- [18] T. Aramoto, F. Adurodija, Y. Nishiyama, T. Arita, A. Hanafusa, K. Omura and A. Morita, Solar Energy Materials and Solar Cells, **75**, 211 (2003)
- [19] Xiangxin Liu, A.D. Compaan, N. Leyarovska, and J. Terry, "Cu K-edge EXAFS in CdTe before and after treatment with CdCl₂," Mat. Res. Soc. Symp. Proc. **763**, paper B3.5, (2003)
- [20] V.G. Karpov, "Critical Disorder and Phase Transitions in Random Diode Arrays," Phys. Rev. Ltrs. **91**, 226806-1 (2003); V.G. Karpov, A.D. Compaan, and Diana Shvydka, "Random diode arrays and mesoscale physics of large-area semiconductor devices," Phys Rev. B **69**, 045325 (2004)
- [21] J. Drayton, C. Taylor, A. Gupta, R.G. Bohn, G. Rich, A.D. Compaan, B.E. McCandless, and D. Rose, "Properties of reactively sputtered ZnTe:N and its use in recombination junctions," 29th IEEE Photovoltaic Specialists Conference-2002, pp. 539-42.
- [22] A.D. Compaan, Jennifer Drayton, V.Y. Parikh, G. Rich, A. Gupta, C. Taylor, Y. Yu, T. Osborn, and R.G. Bohn, Third World Conference on Photovoltaic Energy Conversion, Osaka, May 11-18, 2003 (paper 2P-A8-31).
- [23] S.L. Wang, S.H. Lee, A. Gupta, and A.D. Compaan, "RF sputtered HgCdTe films for tandem cell applications," 11th Int'l Conf. on II-VI Compounds, *physica status solidi (c)*, 1.4.2004, pp.1046-9